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Final Report on

PRODUCTION OF SODIUM AND HYDROGEN-ION CONDUCTING SILICATES BY SPRAY-DRYING

PHASE I

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for

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I INTRODUCTION

This report briefly reviews the work reported in March 1983 and follows this with a summary of progress since that time.

II THE PROCESSING CONDITIONS THAT RESULT IN THE PRODUCTION OF REACTIVE SPRAY-DRIED PRECURSORS OF NGS AND NYS FROM WATER-SOLUBLE REAGENTS

0.1M solutions of Na_2CO_3, $Gd(CH_3COO)_3.6H_2O$ and Na_2SiO_3 were mixed and sprayed into the spray dryer. The liquid was constantly stirred to maintain the precipitates in suspension. The influence of the inlet and outlet temperatures of the spray dryer were monitored and the surface areas of the resultant powders were measured. These results are shown in Table I. More reactive powders result from higher outlet temperatures.

Using these conditions, high-surface-area-precursor powders leading to high quality NGS and NYS ceramics, have been routinely sprayed. Recently, a successful spraying of 0.3M solution has produced acceptable material.

III PRECURSOR POWDER CHARACTERISATION

As mentioned above and listed in Table I, specific surface area of the NGS/NYS powders has been measured on each batch. The degree of crystallinity of these uncalcined powders has not been assessed but their SEM morphology has been studied. An SEM micrograph of NGS precursor powder is shown in Figure 1.

IV CALCINATION OF THE PRECURSOR POWDER

The optimum temperature for calcination of the NGS and NYS precursor powders was determined by thermal analysis (TGA/DTA). Thermograms for NGS are shown in Figure 2. On this figure are also plotted the thermograms for spray-frozen/

Temperatures (°C)		Salts	Surface Areas (m^2/g)
Inlet	Outlet		
210	73	Acetate	24.3
220 ∿ 218	103 ∿ 106	Acetate	20.1
218 ∿ 180	98 ∿ 85	Acetate	38.8
220	110	Acetate	42.4

TABLE I

	Sintering Conditions		f(NGS), f(NYS)	Density(%)
	Temp(°C)	Time(min)		
NGS*)	1030	30	1.0	88.1
	1050	30	1.0	95.4
	1055	30	1.0	97.4
	1062	30	1.0	98.3
	1064	30	1.0	97.3
NYS*)	1140	30	1.0	96.5 *1)
	1140	30	1.0	97.5 *2)

*1) Pellet

*2) Bar

*) These NGS and NYS produced from 0.1 M solutions

TABLE II

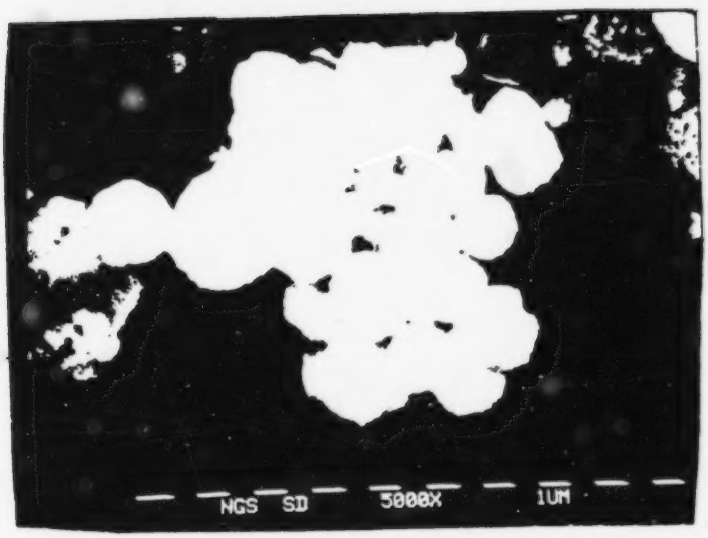

Figure 1

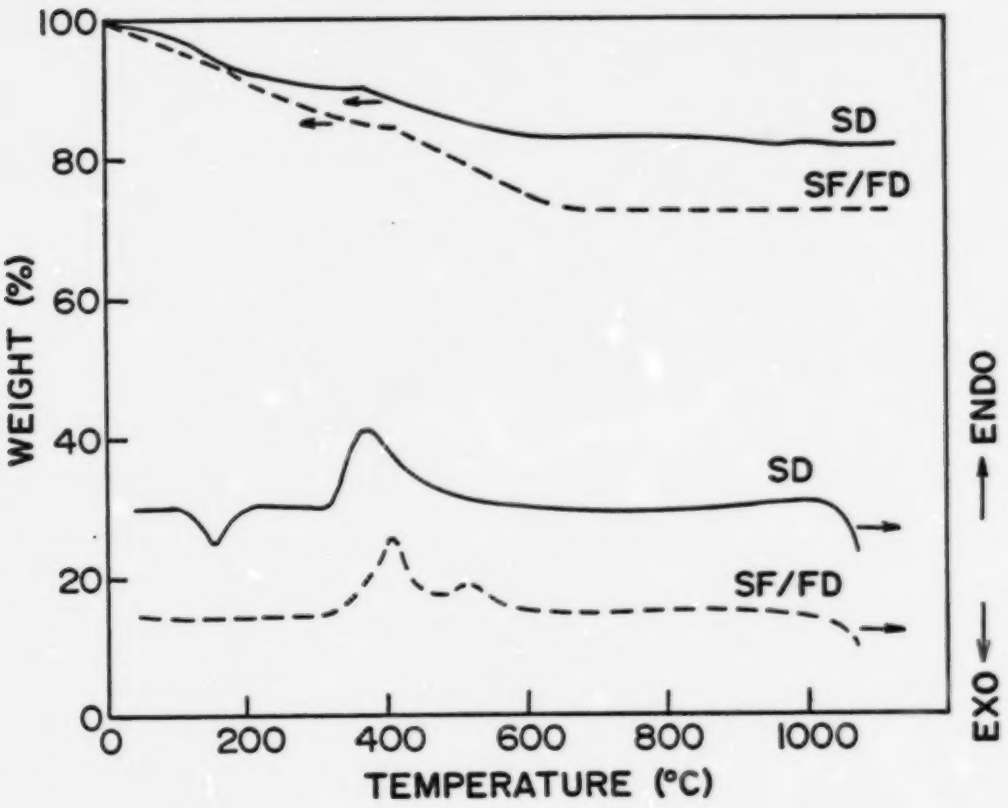
100
80
60
40
20
0
WEIGHT (%)
SD
SF/FD
SD
SF/FD
0
200
400
600
800
1000
TEMPERATURE (°C)
EXO
ENDO

Figure 2

freeze-dried NGS. The loss of Na becomes significant at temperatures $>650^{o}C$ so the calcination range 530^{o}-$600^{o}C$ was chosen. Optimum calcination conditions for NYS were determined to be $620^{o}C$ for 3 hours. The surface area values for the calcines are 9.2 m^2/g (NGS) and (NYS). SEM micrographs of the calcines are shown in Figures 3 and 4. X-ray diffraction analysis of both calcines showed them to be similar to the $Na_3YSi_3O_9$-type structure.

V DEAGGLOMERATION, SHAPING AND SINTERING OF CALCINED POWDERS

Calcines are routinely ball-milled overnight in rubber lined mills with teflon balls. In this way, contamination of the powders is minimised. Bars and pellets are pressed at 3000 psi and isostatically pressed at 50,000 psi and then sintered. The optimum sintering conditions for NGS are $1050^{o}C$/15 mins. and for NYS are $1140^{o}C$/15 mins. These conditions are requisite to produce single-phase sintered NGS and NYS of density $>96\%$ theoretical. XRD analysis was used to determine the phase analysis of the sinters. The level of conducting phase was defined as f(NGS) and f(NYS) for NGS and NYS respectively. These functions are defined as follows;

$$f(NGS) = \frac{I_{2.766\text{Å}(NGS)}}{I_{2.766\text{Å}(NGS)} + I_{2.68\text{Å}(Na_3GdSi_3O_9)}}$$

$$\text{and } f(NYS) = \frac{I_{2.753\text{Å}(NYS)}}{I_{2.753\text{Å}(NYS)} + I_{2.673\text{Å}(Na_3YSi_3O_9)}}$$

assuming that the major impurity phase is $Na_3(Gd\text{-}Y)Si_3O_9$ and I indicates the height of the x-ray diffraction peak at the d-spacing given. For 100% NGS or NYS, the functions equal unity. A series of typical time/temperature/f(NGS) (NYS)/density results are shown in Table 2.

The various processing parameters were correlated and the most consistent correlation that emerged was that between surface area of calcine and the

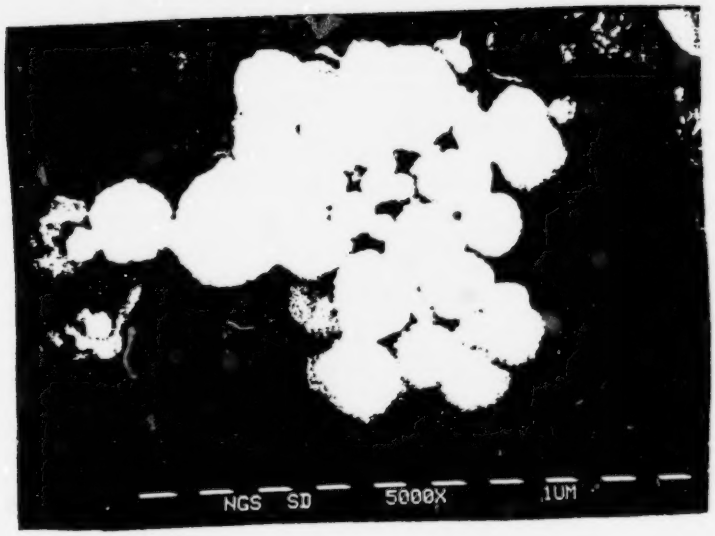

Figure 3

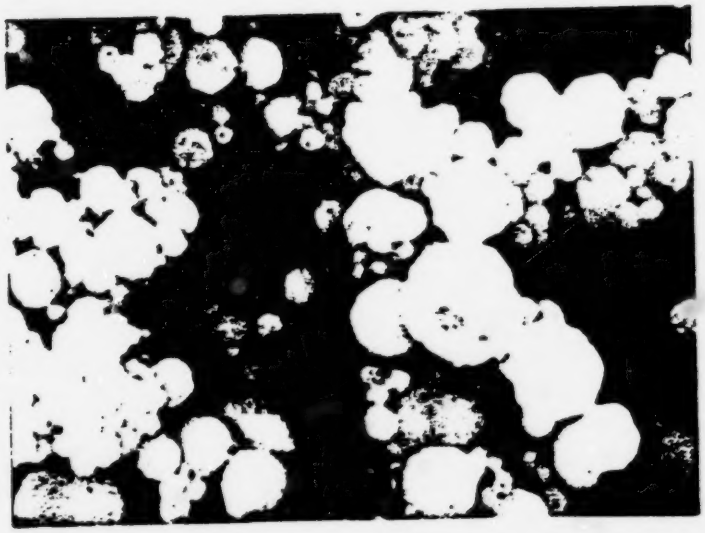

Figure 4

sintered density. It was determined that a minimum surface area of 8 m^2/grams was requisite for > 96%-theoretical sintered density.

VI PROGRESS - MARCH '83-NOVEMBER '83

As reviewed, the two materials of interest have the compositions $Na_5GdSi_4O_{12}$(NGS) and $Na_5YSi_4O_{12}$(NYS). Both of these materials in polycrystalline form have been developed by spray-drying precursor powders (patent filed Yamashita/Nicholson). The sodium ion conductivity of NGS at 300°C is superior to that of B-Al_2O_3 whereas that of NYS is slightly inferior. Of the 96 sodium ions per unit cell of these silicates, 49 are mobile. The balance of the sodium ions reside in the large silicate "towers" which constitute the skeleton of the structure. The skeleton is held together by the rare earth ions cross-linking the towers. The approximately 50% of the sodium ions which are mobile are loosely held around the periphery of the towers and can exchange easily. These mobile sodium ions give these structures their superior three-dimensional conductivity. Direct exchange to the hydronium analogue causes mechanical degradation and so the intermediate potassium exchange step is required. The work here covers a study of the kinetics of this process. During this exchange, the development of surface layer was noted. Our experiments to characterise this process and eliminate the problem are discussed. Finally, field assisted ion exchange of K-NGS and K-NYS in acetic acid has been characterised. Estimates of the hydronium ion conductivity of these ceramics have been made based on diffusivity data and these are compared with the current-voltage data obtained during the ion exchange.

VI-1 Preparation of K-Substituted Material

In a similar manner to B alumina, it is necessary to expand the lattice to allow non-destructive ion exchange to the hydronium analog. This has been carried out using potassium containing chloride melts. For example, a sample of NGS with f(NGS)=0.96 and density=99.3% was immersed in a KCl melt at 800°C. The extent of exchange was followed by measuring the sodium ion concentration in the melt using atomic absorption spectroscopy (Appendix I). The results are shown in Figure 5 where represents the fraction of sodium ions which have been exchanged from the sample. Interestingly, the exchange ceases after approximately 8 hours when just over half the sodium have been exchanged. This is consistent with the fact that only 50% of the sodium ions are mobile. The remainder are immobile and cannot be exchanged. The lattice parameters of NGS and the resultant K-NGS were measured and it was found that the lattice parameter, a, had increased from 22.119 A to 22.144 A whereas the c-axis was unchanged at 12.664 A. The increase is associated with an increase in the distance between the towers where the mobile ions are located and is consistent with the potassium ions only replacing the mobile sodium ions.

As shown in Figure 5, the sample broke into two pieces during this exchange step. This is probably related to the use of pure KCl and it has been shown that a melt composition of 55:45 KCl/NaCl is adequate to accomplish exchange. Such have been utilised without mechanical degradation of the samples. However, a surface layer develops during this exchange step. This can be clearly seen in the EMPA traces shown in Figure 6. This also shows that the potassium ions distribute themselves uniformly throughout the bulk of the sample. In order to determine the composition of the surface layer, a number of samples were immersed

in NaCl/KCl melts with varying compositions. The x-ray powder diffraction patterns of the exchanged material is shown in Figure 7. The peaks for NGS are shown in Figure 7A. Following immersion in KCl for 10 hours the f(NGS) of coarse fragments of the pellet had fallen to 0.62 and some evidence for $Na_3GdSi_3O_9$ peaks have appeared (Figure 7B). Using powder samples, the transformation is more evident (Figures 7C-7F). Following immersion in a melt with a potassium mole fraction, X , of 0.01 for 8 hours, f(NGS) had fallen to 0.56. For a melt with $X = 0.2$, f(NGS) fell to 0.39 in 4 hours and after 24 hours in $X = 0.2$, f(NGS) was 0.29. It took only three hours in 100% KCl to convert the powder to 100% $(K,Na)_3GdSi_3O_9$ (Figure 7F). It is suggested that the reaction involves the formation of a mixed alkali silicate according to:

$$Na_5GdSi_4O_{12} + K^+ \rightleftharpoons (Na,K)_3GdSi_3O_9 + (Na,K)SiO_3$$

Two avenues have been explored to eliminate the formation of this surface layer:

1) the addition of silicate

2) the addition of CsCl

Results of the silicate experiments are summarised in Table III. Clearly this approach is not fruitful probably because the silicate is insoluble in the melt. The second approach involves the addition of CsCl to lower the melt temperature to below 560°C. Using a melt with a cationic (Na:K:Cs) ratio of 0.35:0.35:0.30, successful ion exchange was completed in 9 hours and the resulting sample had an f(NGS)=0.88. This result indicates very little layer formation. This technique will be investigated further.

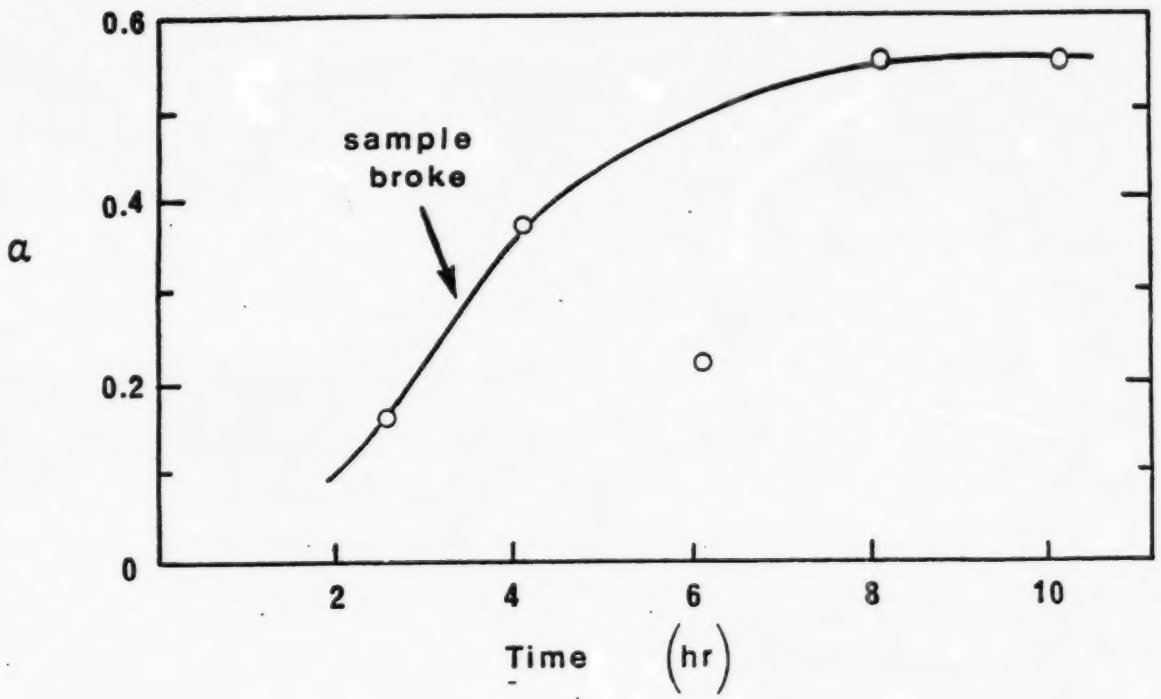

Figure 5 Fraction of Na ions exchanged from NGS by a KCl melt at 800°C as a function of time

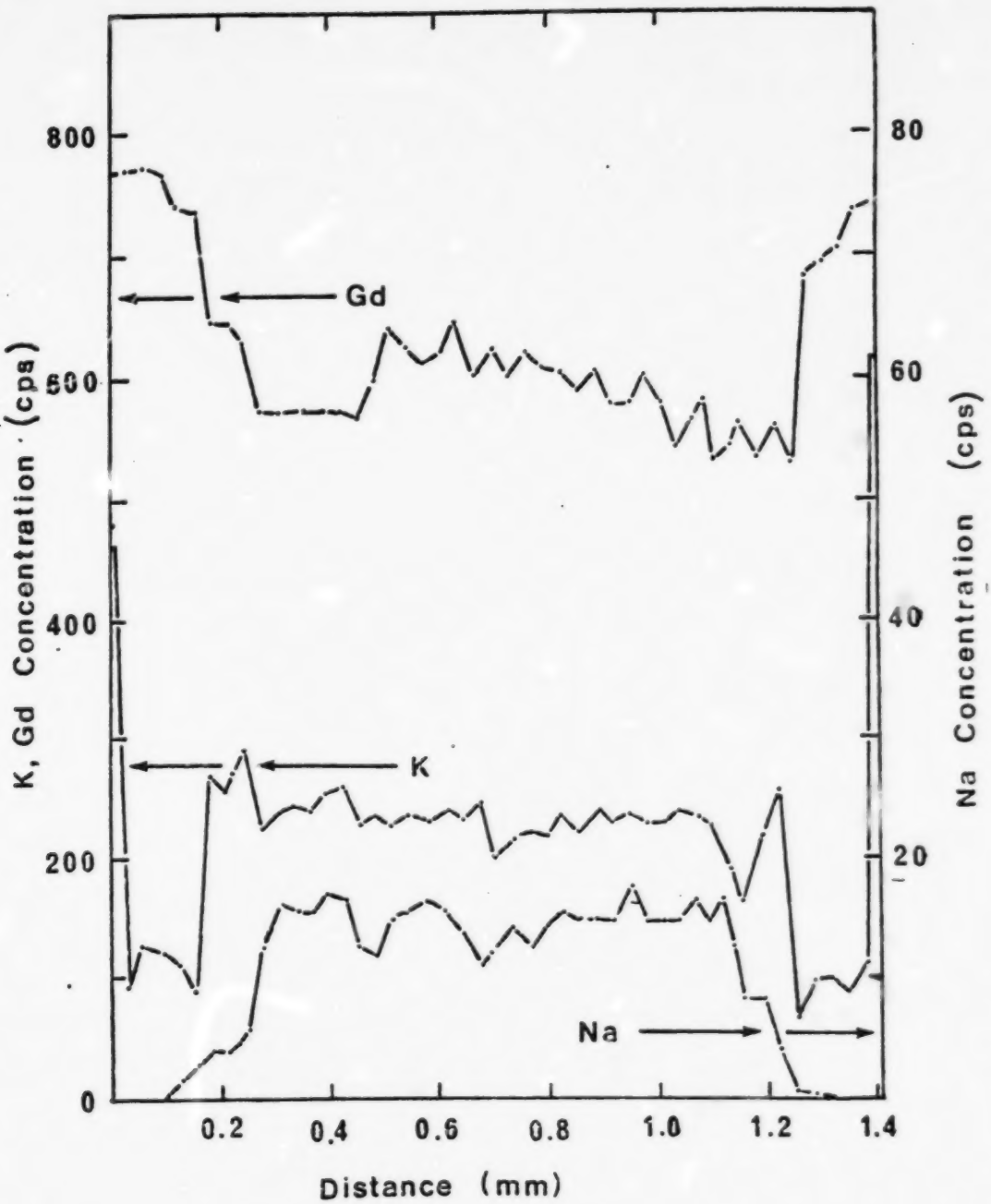

Figure 6 K,Na and Gd distribution profiles obtained by EMPA on NKGS

Table III: Results of silicate addition experiments

Silicate conc. (mole%)	f(NGS) (surface)
0.5	0.43
0.9	0.44
4.7	0.41
9.3	0.41

VI-2 Field Assisted Ion Exchange - Mass Transport

Field assisted K^+ -H_3O^+ ion exchange of silicates was carried out in acetic acid at 80°C. The samples were removed and weighed and the increase in weight was related to the replacement of heavier K^+ by lighter H_3O^+. The diffusivity of H_3O^+ was calculated from:

$$w = 2 C_o \frac{D}{\pi} \sqrt{t} \qquad (1)$$

where C_o is the surface concentration assuming all mobile ion sites are exchanged to H_3O^+, D is the diffusion coefficient, and w is the weight as a function of time. The derivation of this expression is given in Appendix II. The equivalent conductivity is then given by the Nernst-Einstein equation:

$$\sigma_{H_3O^+} = \frac{n q^2 D_{H_3O}}{kT} \qquad (2)$$

Log (T σ) versus 1/T plots for H_3O^+ exchanged NGS and NYS are shown in Figure 8. Shown on the plots are the equivalent resistivities at the temperatures indicated. Values are also given for K^+ ions in KGS extrapolated from higher temperature data using non-blocking (K/Na)NO_3/NO_2 electrodes between 250°C and 320°C. The resistivity of hydronium exchanged 6N3 ceramic aluminas over the same

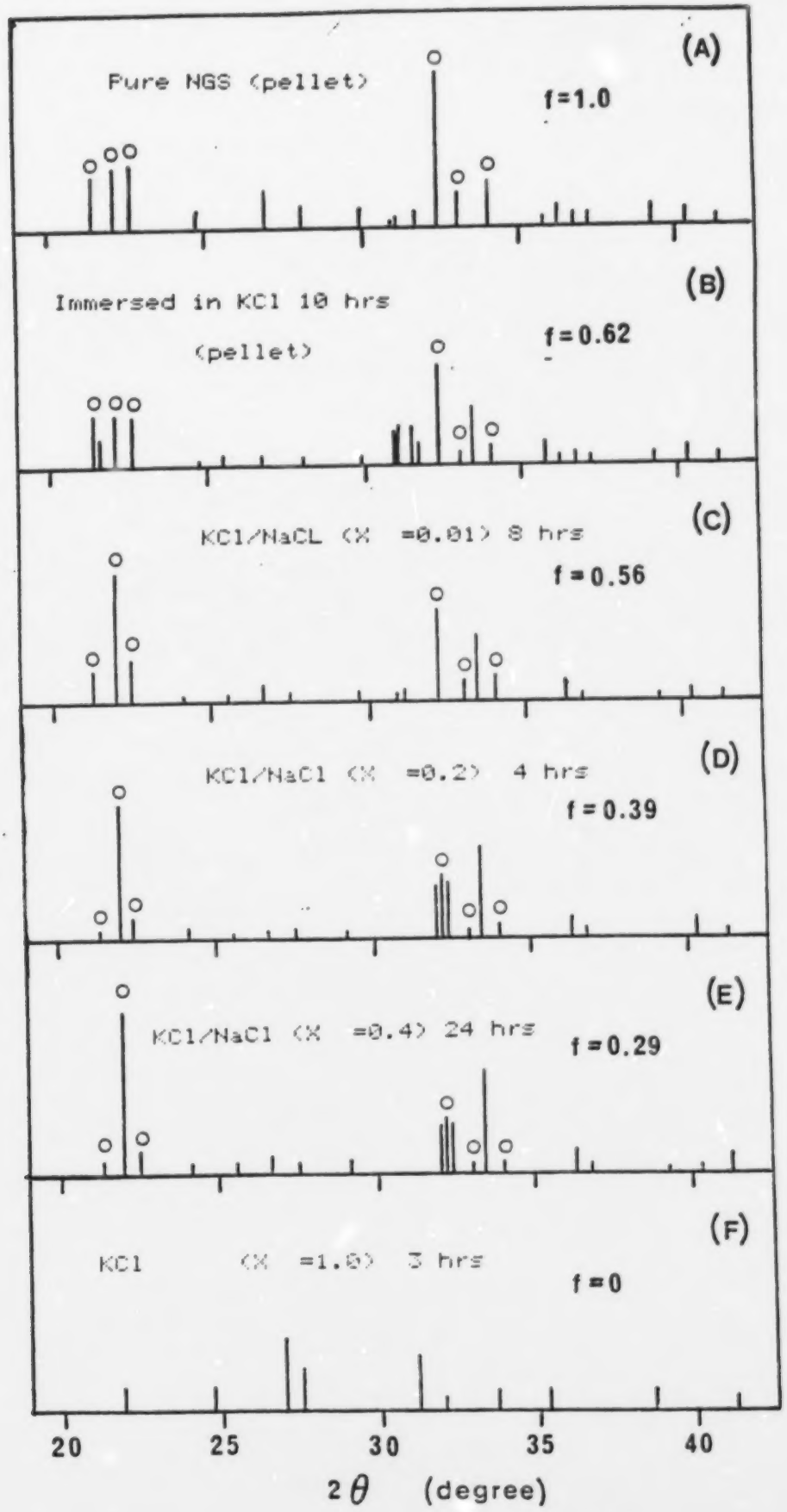

Figure 7 X-ray powder diffraction patterns of exchanged NGS

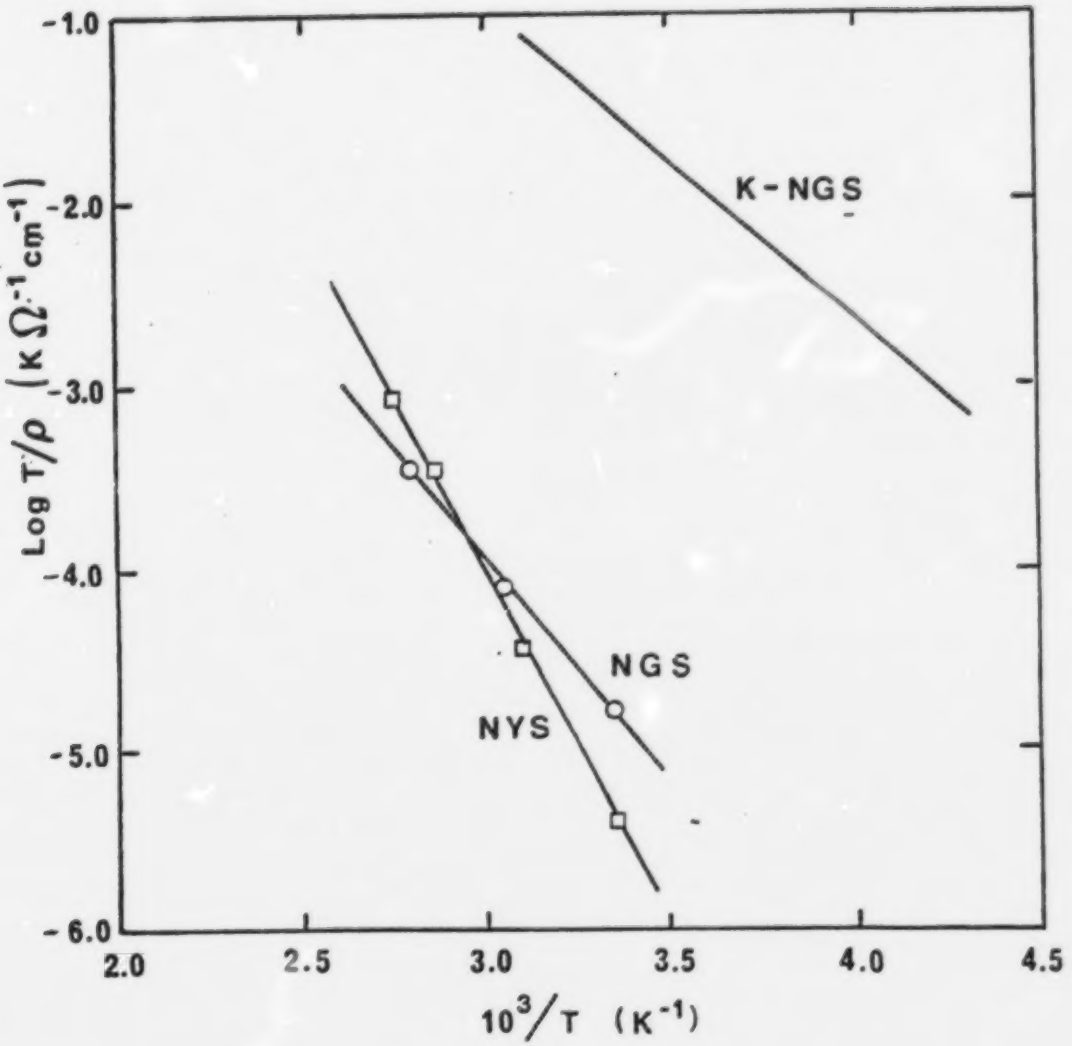

Figure 8 Log (T/ρ) versus 1000/T for hydronium exchanged NGS and NYS and K^+ conductivity in NGS

temperature range (25-100°C) is 9×10^6 to $1.6 \times 10^5 \Omega^{-1}$ cm^{-1} (3).

These results indicate that the conductivity of the silicates is comparable to, and in some temperature ranges, possibly higher than the 6N3 aluminas. The conductivity for H_3O^+ is substantially lower than for K^+. In light of the equal size of the two ions it is possible that the mobile species is $H(H_2O)_N$ where $N \geq 1$ or where the H_2O is chemically bonded by Na-Si-O tower groups. This is to be investigated by infra-red and ultrasonic resonance studies.

VI-3 Field Assisted Ion Exchange - Current/Voltage

Conductivities can also be estimated from I-V measurements and are listed in Table IV.

Table IV

Conductivities estimated from I-V measurements in field assisted ion exchange in acetic acid at 75°C.

Time of exchange hrs	K-6N3	NGS $\Omega^{-1}cm^{-1}$	NYS
1	$7x10^{-7}$	$2.3x10^{-5}$	$9.0x10^{-6}$
2	$4.7x10^{-7}$	$2.0x10^{-5}$	$6.6x10^{-6}$
3	$3.6x10^{-7}$	$1.8x10^{-5}$	$5.9x10^{-6}$
4	$3.1x10^{-7}$	$1.5x10^{-5}$	$4.5x10^{-6}$
5		$1.4x10^{-5}$	$4.1x10^{-6}$
6		$1.3x10^{-5}$	$3.6x10^{-6}$

These conductivities are from whole pellets and essentially examine the exchanged layer. The conductivities are higher than those found in Section VI-2. Further studies will include bulk conductivity measurements using standard impedance methods.

APPENDIX I

Exchange fraction α in NGS

(a) Initial $[K^+]$ in the melt m_o = 10 $\times [Na^+]$ in NGS

(b) M = molecular wt. of NGS: Specimen wt. = w gm

$\delta = [Na^+] / [K^+]$ in melt at time t as measured by atomic absorption.

$x = [Na^+]$: $m = [K^+]$ at time t

(c) Assuming a 1:1 exchange of K^+ for Na^+

$$\delta = \frac{x}{m - x} = \frac{x}{m}$$

and $$x = \frac{\delta}{1 + \delta} m_o \quad \text{or} \quad m = \frac{1}{1 + \delta} m_o$$

(d) If α is the ratio of $[Na^+]$ in the melt to that initially in the NGS

$$\alpha = \frac{\frac{\delta}{(1 + \delta)} m_o}{5w/M}$$

since there are 5 Na^+ per formula unit of $Na_5 GdSi_4 O_{12}$

(e) In the experiment, m_o = 10 $\times [Na^+]$ in NGS

so that $m_o = 10 (5w/M)$ and

$$\alpha = \frac{10 \delta}{(1 + \delta)}$$

APPENDIX II

Diffusion calculation of $D_{H_3O^+}$

For a diffusive process:

- t = time
- w = weight
- = diffusion coefficient
- c = concentration of H_3O^+ at distance x.

$$\frac{dw}{dt} = -D_{H_3O^+} \frac{dc}{dx} \qquad \text{III-1}$$

The solution of Fick's Law 'y' for a planar semi-infinite medium distance x from the interface is

$$C = C_o\left[1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} \exp(-y)^2 \, dy\right]$$

where C_o is the concentration at the surface

$$\text{or} \quad \frac{dc}{dx} = \frac{d}{dx}\left[\frac{2\,C_o}{\sqrt{\pi}}\left(\frac{1}{2\sqrt{Dt}} \exp\left(\frac{-x^2}{4Dt}\right) dx\right)\right]$$

$$\text{or} \quad \frac{dc}{dx} = \frac{C_o}{\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \qquad \text{III-2}$$

If III-2 is substituted into III-1 and III-1 is solved at x=0 then

$$w = \int_0^t \left[\frac{-C_o\,D}{\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right)_{x=o}\right] dt$$

$$\text{or} \quad w = \frac{2\,C_o\sqrt{D}\,\sqrt{t}}{\sqrt{\pi}} \quad \text{(since exponential term =: when } x = 0\text{)}$$